

# Effective forces between colloids at interfaces induced by capillary wave-like fluctuations

H. LEHLE, M. OETTEL and S. DIETRICH

*Max-Planck-Institut für Metallforschung, Heisenbergstr. 3, D-70569 Stuttgart, and  
Institut für Theoretische und Angewandte Physik, Universität Stuttgart, Pfaffenwaldring  
57, D-70569 Stuttgart, Germany*

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**Abstract.** – We calculate the effective force mediated by thermally excited capillary waves between spherical or disklike colloids trapped at a fluid interface. This Casimir type interaction is shown to depend sensitively on the boundary conditions imposed at the three-phase contact line. For large distances between the colloids an unexpected cancellation of attractive and repulsive contributions is observed leading to a fluctuation force which decays algebraically very rapidly. For small separations the resulting force is rather strong and it may play an important role in two-dimensional colloid aggregation if direct *van der Waals* forces are weak.

*Introduction and synopsis.* – The effective forces between rigid objects immersed in a fluctuating medium have attracted a steadily growing interest because their understanding allows one to design and tune them by choosing suitable media and boundary conditions and by varying the thermodynamic state of the medium. Possible applications range from micromechanical systems to colloidal suspensions and embedded biological macromolecules. Accordingly, these fluctuations may be the zero-temperature, long-ranged quantum fluctuations of the electromagnetic fields giving rise to the original Casimir effect [1] between flat or corrugated immersed metallic bodies [2, 3]. Other examples for fluctuation induced long-ranged effective forces between immersed objects involve media such as bulk fluids near their critical point [4], membranes [5] or interfaces [6].

In this work we investigate the latter manifestation of thermal Casimir forces for nanocolloids floating at surface-tension dominated liquid-vapor or liquid-liquid interfaces where they are effectively trapped. In the presence of charges their mutual interactions often exhibit unexpected strong and long-ranged attractions [7] inducing mesoscale pattern formation. However, these unusual patterns, which, e.g., are of interest for optical applications once they are fixed on a solid substrate, appear also for neutral nanocolloids [8]. In spite of some progress [9], the nature of these effective forces between the colloids is not yet fully understood. This pertains in particular to the role of fluctuations for these types of observations.

Therefore the present effort aims at determining the fluctuation induced contribution to these forces generated by the inevitable thermally excited capillary waves of the fluid interface. As a first step the colloids are taken to be spherical or disklike and electroneutral. We shall

pay special attention to the fact that these colloids are of finite size and that, through their surface properties, they exert certain restrictions on the three-phase contact line formed at the intersection of the fluid interface with the colloid surface.

For the idealized situation of a pinned contact line (corresponding to Dirichlet boundary conditions) this problem has already been studied, mostly in the context of membrane-type interfaces [10]; some general results can be inferred also from Ref. [11]. For a pinned contact line and a Gaussian weight for the interfacial height fluctuations these studies yield for the asymptotic decay of the fluctuation induced force  $F(d)$  as function of the center-to-center distance  $d$  between the colloids (i)  $F(d \rightarrow \infty) \propto d^{-1}$  (attractive) if the centers of the colloids are fixed by some external means and (ii)  $F(d \rightarrow \infty) \propto d^{-5}$  (attractive) if the colloids are free to fluctuate vertically. Going beyond this analysis we find that  $F(d \rightarrow \infty) \propto d^{-9}$  (attractive) if, corresponding to the generic situation, the fluctuations of the three-phase contact line are included, governed by a boundary Hamiltonian which is derived from the surface properties of the colloids and of the interface. This highlights the importance of boundary conditions in Casimir problems. In our case they render the long-ranged tail of the effective force virtually unimportant. However, if the colloids approach each other with a surface-to-surface distance  $h \rightarrow 0$  we find that the force increases  $\propto h^{-3/2}$ . Thus for actual systems the fluctuation induced force is effectively short-ranged and therefore it may play an important role in the coagulation of interfacially trapped colloids. This behaviour cannot be captured if the colloid is approximated by an essentially pointlike object as it has been done in Ref. [6]. We shall also discuss experimental possibilities to separate the fluctuation induced forces from the ubiquitous dispersion forces acting in colloidal systems.

*Model.* – We consider an interface between two fluid phases I and II at which two nano- or microscopic colloids are trapped, either spherical with radius  $R$  or disklike with radius  $R$  and thickness  $H$ . Since the weight of such colloids is negligible, the equilibrium (or reference) configuration is the flat interface with the centers of the spherical colloids vertically positioned such that Young’s law holds at the horizontal three-phase contact circle with radius  $r_0 = R \sin \theta$ . Young’s angle is determined by  $\cos \theta = (\gamma_I - \gamma_{II})/\gamma$  where  $\gamma$  is the surface tension of the I/II interface, and  $\gamma_{I[II]}$  the surface tension between the colloid and phase I [II]. For the disks, the contact line is either the upper ( $\theta < \pi/2$ ) or lower ( $\theta > \pi/2$ ) circular edge, so that  $r_0 = R$ . Deviations from the planar reference interface  $z = 0$  are assumed to be small which allows us to use the Monge representation  $(x, y, z = u(x, y)) = (\mathbf{x}, z = u(\mathbf{x}))$  as a parametrization of the actual interface positions. The free energy cost for thermal fluctuations with small gradients around the flat interface is determined by the change in interfacial energy of *all* interfaces (I/II, colloid/I [II]):

$$\mathcal{H}_{\text{tot}} = \mathcal{H}'_{\text{cw}} + \gamma_I \Delta A_I + \gamma_{II} \Delta A_{II} = \frac{\gamma}{2} \int_S d^2x \left[ (\nabla u)^2 + \frac{u^2}{\lambda_c^2} \right] + \gamma_I \Delta A_I + \gamma_{II} \Delta A_{II}. \quad (1)$$

Here,  $\mathcal{H}'_{\text{cw}}$  is the standard capillary-wave Hamiltonian. In eq. (1) the capillary length is given by  $\lambda_c = [\gamma/(\rho_{II} - \rho_I)g]^{1/2}$ , where  $\rho_k$  is the mass density in phase  $k$  and  $g$  is the gravitational constant. The first term in  $\mathcal{H}'_{\text{cw}}$  expresses the energy needed for creating the additional interface area associated with the height fluctuation, the second one the corresponding cost in gravitational energy. Usually, one has  $\lambda_c \gg R$ ; however, care is required in taking the limit  $\lambda_c \rightarrow \infty$  (see below), corresponding to the limit of a vanishing pinning force  $g \rightarrow 0$ . The integration domain  $S$  is given by the plane  $\mathbb{R}^2$  ( $z = 0$ ) minus the enclosed areas  $S_1$  and  $S_2$  of the projections of the contact lines on the first and second colloid, respectively, onto this plane. Thereby the Hamiltonian depends explicitly on the positions of the colloids. In the reference configuration, the projections  $S_i^0$  of the contact lines are the aforementioned circles

with boundary  $\partial S_i^0$  and common radius  $r_0$ . As discussed in the Introduction, in the case of spheres the contact line itself may fluctuate around its reference position with an energy cost which is determined by changes of the projected meniscus area  $S$  and of the interfaces colloid/I,II ( $\Delta A_{I,II} \neq 0$  in eq. (1)) with respect to the reference configuration. We introduce the vertical position of the contact line at colloid  $i$  as a function of a polar angle  $\varphi_i$  defined on  $\partial S_i^0$  by  $f_i \equiv u(\partial S_i^0) = P_{i0} + \sum_{m \geq 1} [P_{im} \cos m\varphi_i + Q_{im} \sin m\varphi_i]$ . The expansion coefficients  $P_{im}$  and  $Q_{im}$  are referred to as multipole moments of the contact line. Furthermore,  $h_i$  is introduced as the fluctuation induced change in vertical position of the colloid centers with respect to the reference configuration. Following Ref. [12], we restrict the integration in  $\mathcal{H}'_{cw}$  to the reference domain  $\mathbb{R}^2 \setminus \bigcup S_i^0$  and expand the remaining energy differences up to second order in  $f_i$  and  $h_i$ , introducing a boundary Hamiltonian  $\mathcal{H}_{b,i}$  so that  $\mathcal{H}_{\text{tot}} = \mathcal{H}_{cw} + \sum_i \mathcal{H}_{b,i}$ :

$$\mathcal{H}_{cw}[u] = \frac{\gamma}{2} \int_{\mathbb{R}^2 \setminus \bigcup S_i^0} d^2x \left[ (\nabla u)^2 + \frac{u^2}{\lambda_c^2} \right], \quad (2)$$

$$\mathcal{H}_{b,i}[f_i, h_i] = \frac{\gamma}{2} \oint_{\partial S_i^0} d\varphi_i (f_i - h_i)^2 = \pi\gamma \left[ (P_{i0} - h_i)^2 + \frac{1}{2} \sum_{m \geq 1} (P_{im}^2 + Q_{im}^2) \right]. \quad (3)$$

The effective force  $F(d) = -\frac{\partial \mathcal{F}}{\partial d}$  as function of the mean local distance between the colloid centers is determined by the free energy  $\mathcal{F}(d) = -k_B T (\ln \mathcal{Z}(d))$ . The partition function  $\mathcal{Z}(d)$  is obtained by a functional integral over all possible interface configurations  $u$  and  $f_i$ ; the boundary configurations are included by  $\delta$ -function constraints, as introduced in Ref. [13]:

$$\mathcal{Z} = \mathcal{Z}_0^{-1} \int \mathcal{D}u \exp \left\{ -\frac{\mathcal{H}_{cw}[u]}{k_B T} \right\} \prod_{i=1}^2 \int \mathcal{D}f_i \prod_{\mathbf{x}_i \in \partial S_i^0} \delta[u(\mathbf{x}_i) - f_i(\mathbf{x}_i)] \exp \left\{ -\frac{\mathcal{H}_{b,i}[f_i, h_i]}{k_B T} \right\}. \quad (4)$$

$\mathcal{Z}_0$  is a normalization factor such that  $\mathcal{Z}(d \rightarrow \infty) = 1$ . We shall discuss two different realizations of the boundary conditions for the contact line (see Fig. 1). (A) The contact lines and the vertical colloid positions fluctuate freely; this corresponds to the physical situation of smooth, spherical colloids. In this case, the integration measure is given by  $\mathcal{D}f_i = \int dh_i \prod_m dP_{im} dQ_{im}$ . (B) The contact lines are pinned in the reference configuration and do not fluctuate with respect to the colloid surfaces. This corresponds to disks or Janus spheres consisting of two different materials. Within the pinning case, we furthermore distinguish the following three physical situations: (B1) The colloid positions are fixed, e.g., by using optical tweezers; thus there are no integrations over the boundary terms. (B2) The vertical positions of the colloids fluctuate freely, so that  $\mathcal{D}f_i = dh_i dP_{i0} \delta(P_{i0} - h_i)$ . (B3) The vertical position and the orientation of the colloids (tilts) fluctuate freely. Up to second order in the tilts this corresponds to  $\mathcal{D}f_i = dh_i dP_{i0} dP_{i1} dQ_{i1} \delta(P_{i0} - h_i)$ . The  $\delta$ -function expresses the pinning condition. All these cases can be discussed conveniently after splitting the field  $u$  of the local interface position into a mean-field and a fluctuation part,  $u = u_{mf} + v$ . The mean-field part solves the Euler-Lagrange equation  $(-\Delta + \lambda_c^{-2}) u_{mf} = 0$  with the boundary condition  $u_{mf}|_{\partial S_i^0} = f_i$ . Consequently the fluctuation part vanishes at the contact line:  $v|_{\partial S_i^0} = 0$ . Then the partition function  $\mathcal{Z} = \mathcal{Z}_{\text{fluc}} \mathcal{Z}_{\text{mf}}$  factorises – due to the Gaussian form of  $\mathcal{H}_{cw}$  – into a product of a fluctuation part independent of the boundary conditions and a mean field part depending on the boundary conditions (which may fluctuate themselves, see the cases (A), (B2), and (B3)):

$$\mathcal{Z}_{\text{fluc}} = \mathcal{Z}_0^{-1} \int \mathcal{D}v \prod_{i=1}^2 \prod_{\mathbf{x}_i \in \partial S_i^0} \delta(v(\mathbf{x}_i)) \exp \left\{ -\frac{\mathcal{H}_{cw}[v]}{k_B T} \right\},$$

$$\mathcal{Z}_{\text{mf}} = \prod_{i=1}^2 \int \mathcal{D}f_i \exp \left\{ -\frac{\gamma}{2k_{\text{B}}T} \sum_i \oint_{\partial S_i^0} d\ell_i f_i(\mathbf{x}_i) (\partial_n u_{\text{mf}}(\mathbf{x}_i)) \right\} \exp \left\{ -\frac{\mathcal{H}_{\text{b},i}[f_i, h_i]}{k_{\text{B}}T} \right\}. \quad (5)$$

The first exponential in  $\mathcal{Z}_{\text{mf}}$  stems from applying Gauss' theorem to the capillary wave Hamiltonian  $\mathcal{H}_{\text{cw}}[u_{\text{mf}} + v]$ . In this term  $\partial_n u_{\text{mf}}$  denotes the normal derivative of the mean-field solution towards the interior of the circle  $\partial S_i^0$ , and  $d\ell_i$  is the infinitesimal line segment on  $\partial S_i^0$ . In the following we provide only the main steps of the subsequent evaluation of both the fluctuation and the mean-field part. For more details the reader is referred to Ref. [14].

*Fluctuation part.* – The fluctuation part appears in all cases introduced above. In the case (B1) it constitutes the full result for the partition function because in that case  $u_{\text{mf}} = 0$  and  $\mathcal{Z}_{\text{mf}} = 1$ . The  $\delta$ -functions in the fluctuation part of the partition function can be removed by using their integral representation via auxiliary fields  $\psi_i(\mathbf{x}_i)$  defined on the interface boundaries  $\partial S_i^0$  [13]. This enables us to integrate out the field  $u$  leading to

$$\mathcal{Z}_{\text{fluc}} = \int \prod_{i=1}^2 \mathcal{D}\psi_i \exp \left\{ -\frac{k_{\text{B}}T}{2\gamma} \sum_{i,j=1}^2 \oint_{\partial S_i^0} d\ell_i \oint_{\partial S_j^0} d\ell_j \psi_i(\mathbf{x}_i) G(|\mathbf{x}_i - \mathbf{x}_j|) \psi_j(\mathbf{x}_j) \right\}. \quad (6)$$

Here, we introduced Green's function  $G(\mathbf{x}) = K_0(|\mathbf{x}|/\lambda_c)/(2\pi)$  of the operator  $(-\Delta + \lambda_c^{-2})$  where  $K_0$  is the modified Bessel function of the second kind. In this form, the fluctuation part resembles 2d screened electrostatics: it is the partition function of a system of fluctuating charge densities  $\psi_i$  residing on the contact circles. For large  $d/r_0$  it can be calculated by a multipole expansion [10]. In this limit and for  $\lambda_c/d \rightarrow \infty$  we find for the fluctuation force:

$$F_{\text{fluc}} = k_{\text{B}}T \frac{\partial}{\partial d} \ln \mathcal{Z}_{\text{fluc}} \rightarrow -\frac{k_{\text{B}}T}{2} \frac{1}{d \ln(d/r_0)} + \mathcal{O}(d^{-3}), \quad \frac{d}{r_0} \gg 1, \quad \frac{d}{\lambda_c} \rightarrow 0. \quad (7)$$

Note, however, that here the limit  $\lambda_c \rightarrow \infty$  is attained slowly with a leading correction term of the order  $1/(d \ln(\lambda_c/r_0))$ , and that in this limit the free energy difference  $\mathcal{F}(d) - \mathcal{F}(\infty)$  is actually ill-defined ( $\mathcal{F}(d) \sim \ln \ln(d/r_0)$ ) and therefore the effective colloidal interaction in case (B1) – fixed colloids and pinned interface – is only meaningful for a finite capillary length  $\lambda_c$  [15], similar to a free two-dimensional interface the width of which is determined by the capillary wave fluctuations and diverges logarithmically  $\sim \lambda_c$ .

In the opposite limit of small surface-to-surface distance  $h = d - 2r_0$  the fluctuation force can be calculated by using the well-known result for the fluctuation force per length  $f_{2\text{d}}(\tilde{h}) = -k_{\text{B}}T \pi/(12\tilde{h}^2)$  between two lines a mean distance  $\tilde{h}$  apart [13], together with the Derjaguin (or proximity) approximation [16]:

$$F_{\text{fluc}} \approx -\frac{\pi k_{\text{B}}T}{12} \int_0^{r_0} dy \frac{1}{\left(h + 2r_0 - 2\sqrt{r_0^2 - y^2}\right)^2} \xrightarrow{r_0/h \rightarrow \infty} -k_{\text{B}}T \frac{\pi^2}{48} \frac{r_0^{1/2}}{h^{3/2}} + \mathcal{O}(h^{-1/2}). \quad (8)$$

This strong increase as  $h \rightarrow 0$  is a consequence of the finite (mesoscopic) size of the colloids and is missed if the colloids are approximated as pointlike objects [6]. It also turns out (see below) that this increase is not cancelled by any mean-field contributions. Thus it constitutes the dominant short-ranged contribution in all cases (A) and (B1)–(B3). For intermediate distances  $d$  between these limits  $F_{\text{fluc}}$  must be evaluated numerically. In eq. (6) the integral over the auxiliary fields  $\psi_i$  can be carried out because they appear only quadratically in the exponent. The resulting determinant is divergent and requires regularisation. However, the derivative of its logarithm with respect to  $d$  (corresponding to the force) is finite and convergent in a numerical analysis (see Refs. [3, 14] for further details). Actual numerical results, which recover the limiting behaviors given by eqs. (7) and (8), are presented in Fig.1.

*Mean-field part.* – The calculation of  $\mathcal{Z}_{\text{mf}}$  (Eq. (5)) requires to determine the solution of the differential equation  $(-\Delta + \lambda_c^{-2})u_{\text{mf}} = 0$  for the (fluctuating) boundary conditions  $u_{\text{mf}}(\mathbf{x}_i) = f_i(\mathbf{x}_i)$  for  $\mathbf{x}_i \in \partial S_i^0$  and  $u_{\text{mf}}(\mathbf{x}) \rightarrow 0$  for  $|\mathbf{x}| \rightarrow \infty$ . We use the superposition ansatz  $u_{\text{mf}} = u_1 + u_2$  where  $u_i = \sum_m K_m(r_i/\lambda_c) [A_{im} \cos m\varphi_i + B_{im} \sin m\varphi_i]$  is the general mean-field solution in  $\mathbb{R}^2 \setminus S_i^0$ . The solution has to match to the boundary conditions at both circles  $\partial S_1^0$  and  $\partial S_2^0$ . This can be achieved by a projection of  $u_2$  onto the complete set of functions on  $\partial S_1^0$ ,  $\{\cos m\varphi_1, \sin m\varphi_1\}$ , and vice versa. Equating this expansion with the multipole moments  $\hat{\mathbf{f}}_i = (P_{i0}, P_{i1}, Q_{i1}, \dots)$  of the values  $f_i(\mathbf{x}_i)$  of the field  $u(\mathbf{x})$  at the contact lines leads to a system of linear equations for the expansion coefficients  $\{A_{im}, B_{im}\}$ . This system can be solved analytically within a systematic  $1/d$  expansion or numerically, observing rapid convergence (even for small  $d$ ), allowing us to truncate the expansions at  $m_{\text{max}} \approx 20$ . The mean field part of the partition function can then be written as

$$\mathcal{Z}_{\text{mf}} = \int \mathcal{D}f_i \exp \left\{ -\frac{\mathcal{H}[u_{\text{mf}}]}{k_{\text{B}}T} \right\} \exp \left\{ -\frac{\pi\gamma}{k_{\text{B}}T} \sum_i (P_{i0} - h_i)^2 \right\}, \quad (9)$$

where  $\mathcal{H}[u_{\text{mf}}]$  is a symmetric quadratic form of the multipole moments of the contact lines,

$$\mathcal{H}[u_{\text{mf}}] = \frac{\gamma}{2} \begin{pmatrix} \hat{\mathbf{f}}_1 \\ \hat{\mathbf{f}}_2 \end{pmatrix}^T \begin{pmatrix} \mathbf{E}_{1\text{self}} & \mathbf{E}_{\text{int}} \\ \mathbf{E}_{\text{int}} & \mathbf{E}_{2\text{self}} \end{pmatrix} \begin{pmatrix} \hat{\mathbf{f}}_1 \\ \hat{\mathbf{f}}_2 \end{pmatrix}, \quad (10)$$

so that the  $d$ -dependent part of  $\mathcal{Z}_{\text{mf}}$  is given by  $\det \mathbf{E}$ . Before discussing the analytic structure of the dependence on  $d$ , we recall that the integration measure  $\mathcal{D}f_i$  differs for the cases (A), (B2), and (B3). In all cases, the large  $d$  expansion of the mean-field part of the partition function (with  $\lambda_c \rightarrow \infty$ ) leads to a repulsive effective force between the colloids:

$$F_{\text{mf}} = k_{\text{B}}T \frac{\partial}{\partial d} \ln \mathcal{Z}_{\text{mf}} \rightarrow \frac{k_{\text{B}}T}{2} \frac{1}{d \ln(d/r_0)} + \mathcal{O}(d^{-3}), \quad \frac{d}{r_0} \gg 1, \frac{d}{\lambda_c} \rightarrow 0. \quad (11)$$

Due to  $\mathcal{Z} = \mathcal{Z}_{\text{fluc}} \mathcal{Z}_{\text{mf}}$  the total effective force is  $F = F_{\text{fluc}} + F_{\text{mf}}$ . The leading terms in  $F_{\text{mf}}$  and  $F_{\text{fluc}}$  (Eqs. (11) and (7)) cancel. The same holds for the first subleading terms, and in the cases (A) and (B3) also for the second-next subleading terms. Due to these cancellations it turns out that in all four cases for large distances the effective force is attractive with the leading term stems from the fluctuation part. This can be summarized as follows ( $\frac{d}{r_0} \gg 1, \frac{d}{\lambda_c} \rightarrow 0$ ):

$$\begin{aligned} F &\rightarrow -\frac{8ak_{\text{B}}T}{r_0} \left(\frac{r_0}{d}\right)^9 \begin{cases} \text{(A)} & \text{no pinning – fluctuating contact line: } a = 1 \\ \text{(B3)} & \text{pinning – colloidal height and tilt fluctuations: } a = 9 \end{cases} \\ F &\rightarrow -\frac{4k_{\text{B}}T}{r_0} \left(\frac{r_0}{d}\right)^5, \quad \text{(B2)} \quad \text{pinning – colloidal height fluctuations} \\ F &\rightarrow -\frac{k_{\text{B}}T}{2} \frac{1}{d \ln(d/r_0)}, \quad \text{(B1)} \quad \text{pinning – fixed colloids.} \end{aligned} \quad (12)$$

In the opposite limit,  $h = d - 2R \rightarrow 0$  the effective mean-field force  $F_{\text{mf}}$  is repulsive. In case (B2) the leading behaviour for  $h \rightarrow 0$  can be estimated analytically [14]:

$$F_{\text{mf}}(h \rightarrow 0) \approx \frac{k_{\text{B}}T}{4h} \quad (13)$$

We find numerically that the inclusion of higher (beyond the zeroth order) multipole moments of the contact line, as relevant for the cases (A) and (B3), slightly changes the prefactor in Eq. (13) but does not alter the  $1/h$  behaviour. The increase of the mean-field force for  $h \rightarrow 0$  is weaker than that of  $F_{\text{fluc}}$  so that for all cases the leading behaviour of the total effective force at small distances is also attractive and given by Eq. (8).

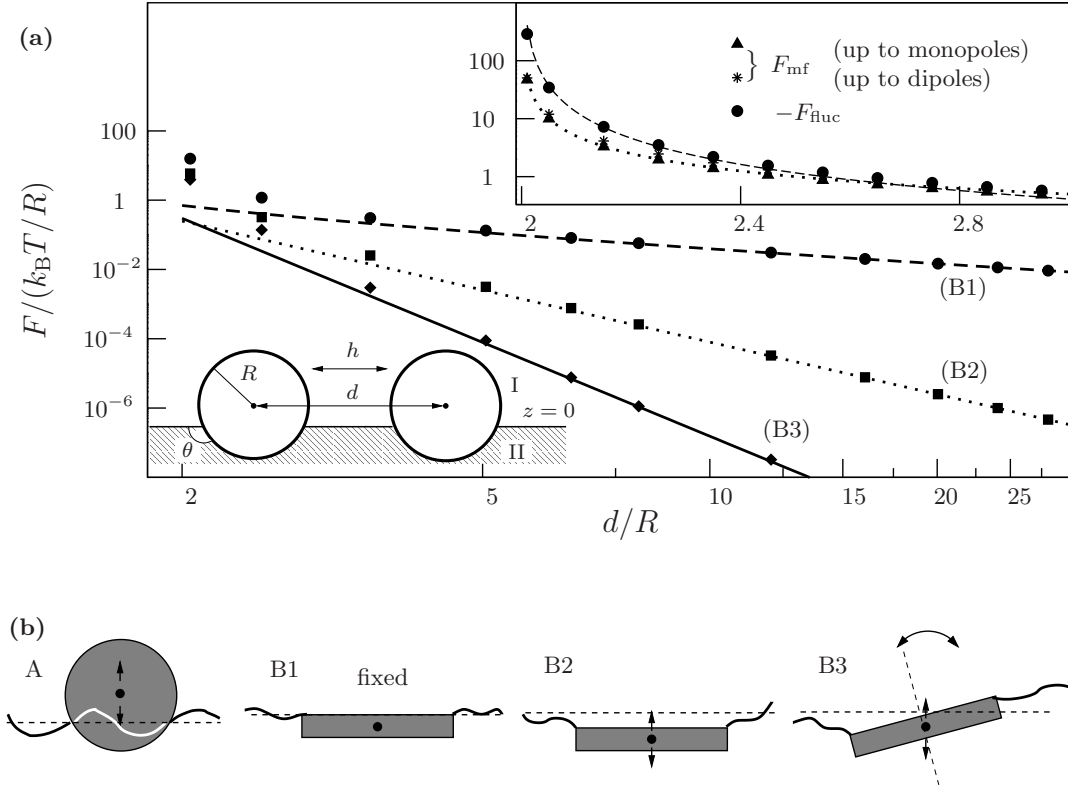


Fig. 1 – (a) Numerically calculated thermal total Casimir force  $F$  (symbols) for various boundary conditions compared with the analytic results in eq. (12) (lines). The inset shows the results for the two contributions to the short range regime: numerically calculated fluctuation contribution ( $-F_{fluc}$ ) and mean-field contribution ( $F_{mf}$ ) compared with the analytic expressions in eqs. (8) (dashed) and (13) (dotted), respectively. (b) Sketch of the various boundary conditions. For (B1)-(B3), the disks may be replaced by Janus spheres.

*Discussion.* – The restrictions which two rotational symmetric colloids trapped at a fluid interface impose on its thermally excited capillary waves, lead to a thermal Casimir force between them. At large separations  $d \gg r_0$  there is an interesting interplay between the attractive interaction due to the interface fluctuations and a repulsive interaction generated by the mean-field contribution to the fluctuating boundary conditions. This results in a cancellation of leading terms up to a certain order in  $1/d$ , which depends on the specific type of boundary conditions. In the opposite limit of small separations  $h = d - 2r_0 \ll r_0$ , the effect of the boundary conditions is much less pronounced, and the resulting force is dominated by  $F_{fluc} \sim h^{-3/2}$  (attractive) compared with  $F_{mf} \sim h^{-1}$  (repulsive), leading to a strong attractive Casimir interaction in this regime (see Fig. 1). Note that for colloid-colloid separations  $h$  of the order of the molecular length scale  $\sigma$  of the fluids, the capillary-wave model is no longer valid. In this limit the total effective force stays finite and can be understood by taking into account the formation of a wetting film around the colloids [17]. At small separations typically also *van der Waals* (vdW) forces become important, leading to a strong tendency of colloid aggregation if not compensated by a repulsive interaction. For spherical colloids at small separations and  $\theta = \pi/2$  the well-known Derjaguin result for



the vdW force is given by  $F_{\text{Derj}}^{\text{vdW}} = -A_{\text{H}}/(12\pi) R/h^2$  where the (effective) Hamaker constant  $A_{\text{H}}$  is determined by the frequency dependent dielectric permittivities of both the colloids and the two fluid phases.  $F_{\text{Derj}}^{\text{vdW}}$  shows an even stronger increase for  $h \rightarrow 0$  and hence will dominate the Casimir force (8) since the Hamaker constant is typically  $A_{\text{H}} \approx 1 \dots 10 k_{\text{B}}T$ . However, refractive index matching between colloids and fluids can result in a significantly smaller value of  $A_{\text{H}}$ . For  $A_{\text{H}}/k_{\text{B}}T < (\pi^3/4)\sqrt{h/R}$  we have  $|F_{\text{fluc}}| > |F_{\text{Derj}}^{\text{vdW}}|$  and therefore in this distance regime an increased influence of the fluctuation induced force on particle aggregation. In the case of two cylindrical disks with height  $H$  the Derjaguin approximation leads to  $F_{\text{Derj}}^{\text{vdW}} \sim -(H/h^2)(R/h)^{1/2}$  if  $h \ll R, H$ . However, for very thin disks ( $H \ll h \ll R$ , c.f. cases (B1)–(B3)), integration over atomic pair potentials  $\sim r^{-6}$ , which give rise to the vdW force, results in

$$F_{\text{td}}^{\text{vdW}} = -A_{\text{H}} \frac{15\pi^2}{48} \frac{H^2}{h^2} \sqrt{\frac{R}{h}} \frac{1}{h}. \quad (14)$$

For these systems  $F_{\text{vdW}}/F_{\text{fluc}} = 15(A_{\text{H}}/k_{\text{B}}T)(H/h)^2 \ll 1$ , so that for  $H \ll h \ll R$  the driving mechanism for flocculation is entirely given by the fluctuation induced force. Thus, the fluctuation induced force can strongly enhance the tendency of colloids at interfaces to flocculate. This effect is independent of material parameters, as long as the system is in the capillary wave regime, i.e., for  $h \gg \sigma$ . In order to discriminate the fluctuation induced force from the vdW force we propose three experimental scenarios. The first one is to weaken the vdW force by lowering the Hamaker constant via index matching which increases the importance of the fluctuation force. Second, for thin disks, the fluctuation induced force dominates, independent of the dielectric properties of the materials. A third mechanism consists of reducing the vdW force by a light polymer coating of the colloids so that in eq. (8)  $h = h_{\text{sts}}$  is given by the surface-to-surface distance between the polymer shells, whereas the distance  $h = h_{\text{core}} > h_{\text{sts}}$  between the cores of the two colloids enters into  $F_{\text{Derj}}^{\text{vdW}}$ . Thus for a sufficiently thick polymer shell the fluctuation induced force will be the dominant interaction at small distances.

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